

FORMATION OF ULTRA-FINE PARTICULATE MATTER FROM PULVERIZED COAL COMBUSTION

C.L. Senior and T. Panagiotou
Physical Sciences Inc.
Andover, MA 01810

Adel F. Sarofim
University of Utah
Salt Lake City, UT

Joseph J. Helble
University of Connecticut
Storrs, CT

KEYWORDS: PM2.5, coal-fired, power plants, fine particulate matter

INTRODUCTION

Although attention is focused currently on the emission of particles less than 2.5 microns (PM2.5) from stationary combustion systems, ultrafine or submicron particulate matter may prove to be an important constituent of PM2.5. Field observations¹⁻³ and theoretical considerations⁴ lead us to conclude that vaporization and condensation of ash occurs in pulverized coal-fired power plants. Furthermore, many toxic trace elements are enriched in the vaporization mode of the fly ash⁵ because many of the inorganic elements in coal are volatile at flame temperatures.^{6,7} In the flame zone, the inorganic vapors homogeneously nucleate to form an ultrafine aerosol with a primary particle size of 0.01 to 0.03 μm .⁸ Post-flame, the combustion gases cool rapidly to near room temperature in a time period of 2 to 5 s. The mean particle size of this condensation aerosol grows by coagulation. Calculations for a typical vapor loading show that the peak of the mass distribution grows to 0.03 to 0.07 μm in the range of 1 to 10 s.⁶ These ultrafine ash particles are not collected as efficiently by electrostatic precipitators as are the larger ash particles.⁹ Thus, toxic metals in the vaporization mode can be preferentially emitted to the atmosphere.

Measurements of submicron aerosol from full-scale coal-fired power plants show a distinct peak in the mass distribution falling in the range of 0.07 to 0.15 μm .^{1-3,9} These measurements are made at the ESP inlet, not in the flame zone. In one study,³ two submicron modes were observed with peak diameters at 0.07 microns and 0.4 μm . Scanning electron micrographs of the two submicrometer modes showed that the 0.4 μm particles were solid spheres, while the particles below 0.1 μm were agglomerates of ultrafine primary particles. In full-scale combustion systems, therefore, ash collected with diameters less than 0.1 to 0.2 μm could be attributed to vaporization.

The ultrafine mode can be ascribed to a vaporization-condensation mechanism.⁴ Taking into account all the observations mentioned above, the ultrafine mode has a peak (mass distribution) of 0.07 to 0.15 μm . The variation in the diameter is mostly due to the combustion conditions; coal type is a second order effect. This can be seen in the data of McElroy et al.² Six power plants of different designs were sampled. All but one were burning western sub-bituminous coals. Data are given on the fraction of the ash found in the submicron aerosol as a function of NO content in the exhaust gas (Figure 1). Since NO is related to the peak combustion temperature, Figure 1 shows that the combustion conditions have a strong effect on the amount of mass in the ultrafine mode. The type of coal and furnace design do not seem to have a strong influence on the amount of ash in the ultrafine mode. Although, it should be noted that while this data set represents most types of boilers (except cyclone-fired), five out of six of the coals are western sub-bituminous coals.

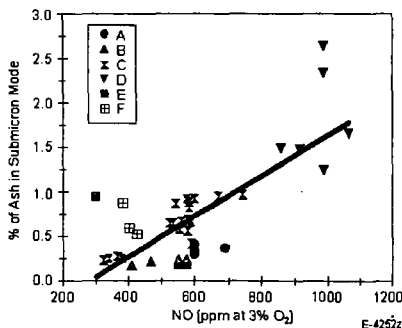


Figure 1. Mass fraction of ash in submicron mode as a function of NO for six different boilers.² Line is best fit ($r^2 = 0.57$).

The composition of the submicron mode from coal combustion varies with coal type. The most complete dataset is found in Quann and Sarofim.¹⁰ This work was both experimental and theoretical. The effects of coal rank, particle size, particle temperature and oxygen concentration were examined.

Also, a theoretical analysis on vaporization from included, excluded and atomically dispersed minerals was accomplished. This analysis indicates that the element vaporization depends on one or more of the following parameters: bulk oxygen concentration, coal rank, coal type, particle size and composition of inherent ash. Results of this effort for Si, Ca and Mg were in very good agreement with the experiments.

MODEL FORMULATION

In the present work, we used the theoretical framework of Quann and Sarofim¹⁰ to calculate the fraction of individual metal oxides (f_i) which vaporize during combustion of the char particle burning for time t_b . The total amount of metal oxides vaporized was then calculated by summing over all the major oxides. For this work, instead of calculating f_i/t_b from first principles, we used existing experimental results as reference, as described in Reference 10. The reference data were values for the fractional vaporization of a metal normalized to the char burnout time, $(f_i/t_b)_r$, the equilibrium partial pressure of the metal, p_{ir} , the concentration of the element of interest in the coal particle, C_{or} , and the coal particle radius (or diameter), r_{or} (d_{or}) for one bituminous and one low rank coal. The reference combustion conditions were a gas temperature of 1750 K and a bulk oxygen partial pressure of 0.2. The particle temperature under such combustion conditions was measured to be 2100 K.¹⁰ The following equations that use reference data were derived from Reference 10. For an element i found in mineral inclusions in the char particles:

$$f_v/t_b = (f_v/t_b)_r (p_i/p_{ir}) (r_{or}/r_o) (C_{or}/C_o) \quad (1)$$

For an element i found primarily organically-bound to the char:

$$f_v/t_b = (f_v/t_b)_r (p_i/p_{ir}) (r_{or}/r_o)^2 (C_{or}/C_o) \quad (2)$$

For an element i found in excluded mineral particles, not contained in char:

$$f_v/t_b = (f_v/t_b)_r (r_{or}/r_o)^2 (C_{or}/C_o) \quad (3)$$

The burnout time was computed assuming diffusion-limited combustion where the burnout time is proportional to the particle radius and the bulk oxygen concentration, p_{O_2} :

$$t_b \propto r_o^2 / \ln(1 + p_{O_2}) \quad (4)$$

The metal gaseous mole fractions, p_i and p_{ir} , are calculated by assuming that the metal oxides undergo reduction during evaporation, for example:



And the partial pressure of SiO is equal to:

$$p_{\text{SiO}} = (a_{\text{SiO}_2} K_{eq} p_{\text{CO}})^{1/2} \quad (6)$$

where a_{SiO_2} is the activity coefficient and K_{eq} is the equilibrium constant. The activity coefficient is assumed to be independent of coal type and combustion conditions, so it cancels out in Eqs. (1) through (3). The equilibrium constants used were curvefits from data over a temperature range of 1500 to 2500 K as shown in Table 1.

The simple equilibria between CO and CO₂ can be used for each metal species of interest, assuming that oxygen diffusing to the char particle surface is completely consumed and that CO is

Table 1. Vaporization Equilibrium Equations and Equilibrium Coefficients - Equilibrium Constants at Temperature Char Temperature T are Calculated from $\ln(K) = A + B/10^4 T$

Vaporization Equation	A	B
$\text{Na}_2\text{O} + \text{CO} = 2\text{Na} + \text{CO}_2$	17.8966	-2.8487
$\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$	11.4942	-4.2064
$\text{SiO}_2 + \text{CO} = \text{SiO} + \text{CO}_2$	18.8256	-5.9700
$\text{Al}_2\text{O}_3 + 2\text{CO} = \text{Al}_2\text{O} + \text{CO}_2$	24.0505	-11.3361
$\text{MgO} + \text{CO} = \text{Mg} + \text{CO}_2$	14.4976	-5.4094
$\text{CaO} + \text{CO} = \text{Ca} + \text{CO}_2$	13.2182	-6.1507

the only product of combustion. In this case, the bulk oxygen concentration, $p_{O_{2b}}$, will determine the concentration of CO at the surface:

$$P_{CO_s} = 2 p_{O_{2b}} / (1 + p_{O_{2b}}) \quad (7)$$

The fraction of potassium vaporized was calculated from a separate equation, based on previous work which showed a good correlations between the fraction of potassium and sodium vaporized during coal combustion.¹²

$$f_{v-K} = 0.007706 + 0.6165746 f_{v-Na} \quad (8)$$

RESULTS

For validation purposes, we used our model to predict metal vaporization from a variety of coals burning at different conditions. Subsequently, we compared our predictions with experimental data. The purpose of this effort was to assess the accuracy of our model with respect to parameters that affect vaporization and then improve the accuracy by making proper corrections. The following parameters that affect the vaporization were examined: (a) the coal type, (b) the coal rank, (c) the coal particle diameter, (d) the oxygen concentration and (e) the element concentration in the coal. A complete set of vaporization data that involved a variety of coals, particle sizes and combustion conditions was given in Reference 10. In those experiments, vaporization from excluded minerals was negligible. Therefore, in our calculations we only accounted for vaporization from included and organically bound minerals.

Initially we calculated the fraction of Si, Na, K, Ca, Fe, Al and Mg that vaporized as oxides, namely: SiO_2 , Na_2O , K_2O , CaO , FeO , Al_2O_3 and MgO . Subsequently, the amounts of the individual amounts of vaporized oxides were estimated. Finally, the amounts of oxides vaporized were summed to get a calculated value of the total ash vaporized. As reference values for Eqs. (1) and (2), the following experimental data we used: (a) for vaporization of Na, Si, Fe and Al from bituminous coals, we used data for Illinois 6 from Quann,¹⁰ and (b) for vaporization of Na, Si, Fe, Al, Ca and Mg from sub-bituminous coals and lignites, we used data for Montana Savage lignite from Quann.¹⁰

Vaporization of major elements was predicted for Illinois 6 considering different coal particle sizes and bulk oxygen contents. Figure 2 shows the effect of oxygen concentration on vaporization from coal particles with diameters of 50 μm and 120 μm with a gas temperature of 1750 K. The model does a good job of predicting the effect of oxygen content on total vaporization. However, the effect of coal particle diameter is not modeled as well. Vaporization for large coal particles is over-predicted by two to three times.

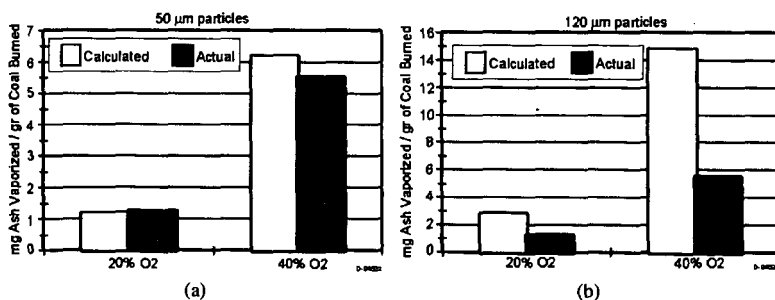


Figure 2. Effect of oxygen concentration on ash vaporization from Illinois 6 coal particles burning at a gas temperature of 1750 K for two different coal particle diameters: (a) 50 μm and (b) 120 μm .

Similar results were obtained for other bituminous coals. Figure 3 compares the amount of vaporization from 50 μm coal particles burning at a gas temperature of 1750 K for the Illinois 6 coal with two other bituminous coals. In Figure 4, the predicted and measured compositions of one of the bituminous coals are shown. The calculation tends to over-predict the amount of iron in the submicron ash for bituminous coals.

Vaporization of major elements was predicted for a Montana lignite considering different coal particle sizes and bulk oxygen contents. Figure 5 shows the effect of oxygen concentration on vaporization from low rank coal particles with diameters of 60 μm and 120 μm with a gas temperature of 1750 K. The model does a good job of predicting the effect of oxygen content and coal particle size on total vaporization.

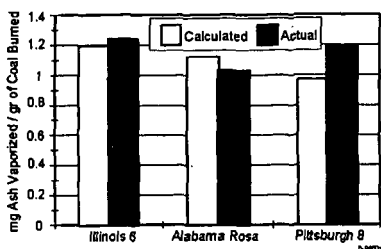


Figure 3. Predicted and measured ash vaporization from bituminous coals: 50 μ m diameter particles burning in 20% oxygen with a gas temperature of 1750 K.

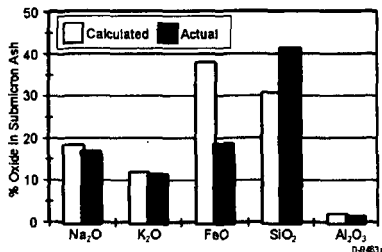


Figure 4. Predicted and measured submicron ash composition from combustion of Pittsburgh 8 coal: 50 μ m diameter particles burning in 20% oxygen with a gas temperature of 1750 K.

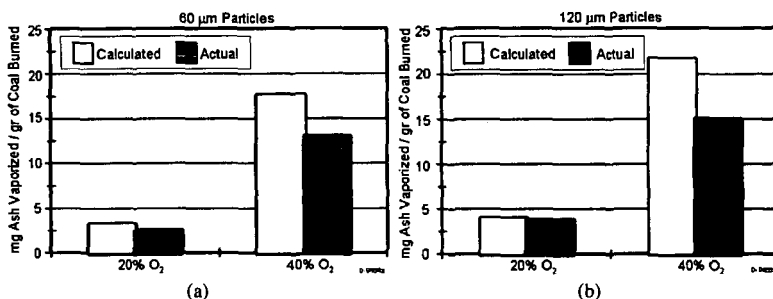


Figure 5. Effect of oxygen concentration on ash vaporization from Montana Savage lignite particles burning at a gas temperature of 1750 K for two different coal particle diameters: (a) 60 μ m and (b) 120 μ m.

Similar results were obtained for other low rank coals. Figure 6 compares the amount of vaporization from 60 μ m coal particles burning at a gas temperature of 1750 K for the Montana Savage lignite (MO SVG L) coal with three other coals: Montana Rosebud sub-bituminous (MO RSB S), North Dakota Lignite (ND L), and Montana Powder River Basin sub-bituminous (MO PRB S).

SUMMARY

This work aimed to develop a model that predicts the vaporization of metals during coal combustion. The model is based on other existing models, experimental data and correlations of data. The main factors that affect the metal vaporization are: the coal rank, the coal type, the coal particle size, the oxygen content (and therefore the particle temperature) and the metal concentration in the coal. Our model predicts fairly accurately the amounts of ash that vaporizes and the submicron ash composition of bituminous coals based on a fixed reference condition. The effect of oxygen concentration and the metal composition of the coal on the ash vaporization are predicted well, but the effect of the coal particle diameter is not predicted accurately. Our model predicts fairly accurately the amounts of ash that vaporizes and the submicron ash composition from a variety of low rank coals based on a fixed reference condition. The model predicts the effect of coal particle size on the ash vaporization better than it does the effect of oxygen concentration, unlike the case of the bituminous coals. The modeling efforts should concentrate on the following areas: (a) the effects of coal particle size and oxygen concentration on the element evaporation and (b) the accuracy of iron and alkali vaporization.

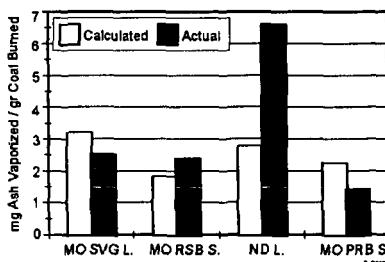


Figure 6. Predicted and measured ash vaporization from low rank coals: 60 μ m diameter particles burning in 20% oxygen with a gas temperature of 1750 K. With the exception of the North Dakota lignite, the model accurately predicts the vaporization of major elements.

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